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Vinyl Polymerization. 215.[†] Decomposition of p-Methoxy-p'-nitrobenzoyl Peroxide in Monosubstituted Benzenes and Polymerization of Styrene Initiated with This Peroxide

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SUMMARY

The rate constant of decomposition of p-methoxy-p'-nitrobenzoyl peroxide (MN-BPO), k'_d , in various monosubstituted benzenes was measured. The value of k'_d seemed to increase with the polarity of the solvents. Activation energies and activation entropies of the decomposition were determined. When styrene was present, the rate constant of decomposition of MN-BPO, k_d , increased markedly by three to five times, except in the case of cyano- and nitrobenzenes.

Polymerization of styrene initiated by MN-BPO in the above-mentioned solvents was carried out. It was found that k_d varied with the kind of solvent, while R_p was almost constant, except in the case of nitro- and iodobenzene. The mechanism for the decomposition of MN-BPO with iodobenzene is discussed.

[†]214 of the series: M. Imoto and K. Ohaski, *Makromol. Chem.*, **117**, 117 (1968).

INTRODUCTION

Leffler [1] studied the decomposition of p-methoxy-p'-nitrobenzoyl peroxide (MN-BPO) in several solvents and concluded that, when benzene was used as solvent, the decomposition proceeded through homolysis, but when acetone, nitrobenzene, or other polar solvents were used, decomposition proceeded through heterolysis. Denney and co-workers [2] studied the rearrangement of MN-BPO labeled with ^{18}O at the carbonyl oxygen of p-methoxybenzoyl or p-nitrobenzoyl group in thionyl chloride, and also concluded that heterolysis of MN-BPO is the first step of the reaction.

On the other hand, we confirmed recently [3] that the polymerization of styrene initiated with MN-BPO in benzene, acetone, or dimethylformamide proceeded through a radical mechanism.

The present paper deals with the effect of the solvent on the rate of the decomposition of MN-BPO. Nine kinds of monosubstituted benzene were used as solvent. The initiation efficiency of the polymerization of styrene initiated by MN-BPO in these solvents was also measured.

EXPERIMENTAL

Preparation of MN-BPO

MN-BPO was synthesized and purified as described in a previous paper [3]; mp 114°C (dec.). Styrene and solvents were purified in the usual manner.

Measurement of the Rate of Decomposition

After charging MN-BPO, solvent, and styrene, the tube was cooled in a dry-ice-methanol bath, flushed several times with oxygen-free nitrogen, and sealed under vacuum. Decomposition was carried out in a thermostat with shaking. The tubes were taken out at definite intervals. The amount of peroxide remaining was measured by iodometry, according to the method of Bartlett and Nozaki [4].

Polymerization Procedure

After charging monomer, peroxide, and solvent, the glass tube was cooled in a dry-ice-methanol bath, flushed several times with oxygen-free nitrogen, and sealed under vacuum. Polymerization was carried out in a

thermostat with shaking. The tubes were taken out at definite intervals and the contents were poured into an excess of methanol to isolate the polymer.

Degree of polymerization of polystyrene was calculated by the following equation [5]:

$$P_n = 1770 [\eta]^{1.40} \quad (\text{in benzene, } 30^\circ\text{C})$$

RESULTS AND DISCUSSION

The Rate of Decomposition of MN-BPO

The decomposition of MN-BPO was carried out at 70°C , where the initial concentration of the peroxide was kept constant at $5 \cdot 10^{-2}$ moles/liter. As shown in Fig. 1, the plots of the amount of MN-BPO decomposed against time did not, in some cases, go through the origin. The experiments were proved to be reproducible. There may be little reason to doubt that a bimolecular reaction of MN-BPO with solvent proceeded together with a monomolecular decomposition of the peroxide.

$$-\frac{d[\text{MN-BPO}]}{dt} = k_2 [\text{MN-BPO}] [\text{solvent}] + k_1 [\text{MN-BPO}]$$

The former reaction may be ionic or of the electron-transfer type, and the latter homolytic spontaneous decomposition. The phenomenon was not observed for the decomposition of unsubstituted BPO. It has been shown that MN-BPO is more liable to decompose heterolytically than unsubstituted BPO, as cited in the literature [1]. Thus, MN-BPO could give such an anomalous plot. We calculate the rate of decomposition of MN-BPO (R_d') here, simply assuming that the apparent rate of decomposition is determined by the slope of the straight lines in Fig. 1.

$$R_d' = k_d' [\text{MN-BPO}] \quad (\text{in the absence of styrene})$$

The rate constants of decomposition thus obtained, k_d' , together with the values of dielectric constants, ϵ , of the solvents are listed in Table 1. The values of k_d' seemed to increase with dielectric constants of the solvents. The value of $k_d' = 2 \times 10^{-5}$, which was found in benzene at 70°C , was in fair agreement with the one calculated from the data obtained for the decomposition of symmetrically substituted benzoyl peroxides by O'Driscoll and White [6].

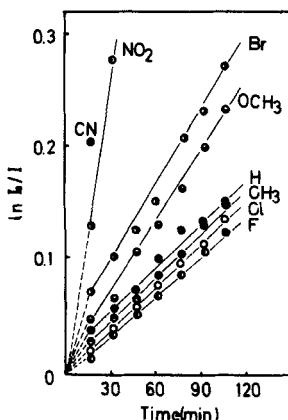


Fig. 1. Decomposition of MN-BPO in several monosubstituted benzenes at 70°C. I_0 : the initial concentration of MN-BPO (5×10^{-2} moles/liter); I : the concentration of MN-BPO remaining.

Table 1. Decomposition of MN-BPO at 70°C

Solvent	$k_d^b \times 10^5 \text{ sec}^{-1}$	$k_d^c \times 10^5 \text{ sec}^{-1}$	ϵ
Anisole	3.75	10.0	4.30
Toluene	2.28	8.5	2.28
Benzene	1.98	9.0	2.27
Fluorobenzene	1.98	11.0	5.42
Chlorobenzene	2.14	10.8	5.61
Bromobenzene	3.61	10.0	5.39
Cyanobenzene	23.33	20.0	25.2
Nitrobenzene	17.22	11.8	34.6
Iodobenzene	very fast	—	4.63

^a [Styrene] = 4.36 moles/liter.

^b k_d' is the rate constant in the absence of styrene.

^c k_d is the rate constant in the presence of styrene.

Next, the decomposition of MN-BPO was carried out, varying the temperature between 65 and 80°C, and the activation energies of decomposition were calculated by the Arrhenius equation. The activation entropies were also calculated at 70°C. As Fig. 2 shows, the compensation rule was found to be established between the values of activation energy and activation entropy.

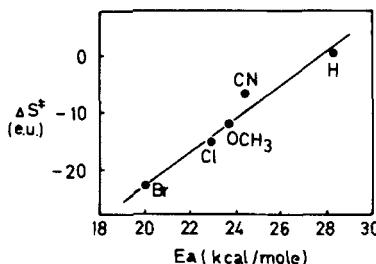


Fig. 2. Relationship between activation energies and activation entropies.

The Rate of Decomposition of MN-BPO in the Presence of Styrene

The rate of decomposition of MN-BPO was measured in the presence of styrene at 70°C. The concentration of styrene was the same as that shown in the next section, which deals with the rate of polymerization. The results obtained are listed in Table 1.

As shown in Fig. 3, the plots of the amount of MN-BPO decomposed against time went through the origin. A very interesting result that was found is that the presence of styrene increased the rate of decomposition of MN-BPO except for cyano- and nitrobenzene.

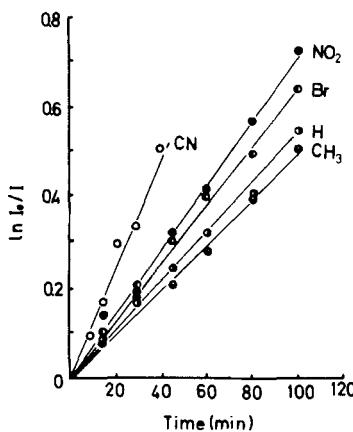


Fig. 3. Decomposition of MN-BPO in monosubstituted benzenes at 70°C in the presence of styrene. $I_0 = [\text{MN-BPO}]_0 = 5.2 \times 10^{-2}$ moles/liter; $[\text{styrene}] = 4.36$ moles/liter. The lines for F, Cl, and OCH₃ were omitted because they overlapped above the line for Br.

Table 2. Initiator Efficiency of MN-BPO
in the Presence of Styrene at 70°C

Solvent	$R_p \times 10^5$ moles/liter sec	f	$f \cdot k_d \times 10^5$
Anisole	2.37	0.13	1.31
Toluene	2.12	0.14	1.19
Benzene	2.27	0.13	1.17
Fluorobenzene	2.11	0.10	1.05
Chlorobenzene	2.29	0.11	1.20
Bromobenzene	2.29	0.12	1.23
Cyanobenzene	2.45	0.07	1.40
Nitrobenzene	0.08	~0.00	0.00
Iodobenzene	0.0	—	—

^a [MN-BPO] = 2.97×10^{-3} moles/liter, [styrene] = 4.36 moles/liter.

Needless to say, the rate of decomposition of unsubstituted BPO was suppressed by the presence of styrene; the cause of this phenomenon was considered to be the disappearance of the induced decomposition. The reason for the increased rate of decomposition of unsymmetrically substituted MN-BPO in the presence of styrene is still obscure and is under investigation.

Polymerization of Styrene

Polymerization of styrene initiated by MN-BPO was carried out in the solvent mentioned above at 70°C, where the initial concentrations of the MN-BPO and styrene were kept constant at 2.97×10^{-3} and 4.36 moles/liter, respectively. The initial rates of polymerization, R_p , were determined from the time-conversion curves. From R_p and k_d values, the efficiency of initiation, f, was calculated, using Tobolsky's equation for styrene, where $A = 6.10 \times 10^{-6} \exp(12.61 \text{ kcal/RT})$ [7].

$$f = R_p^2 \frac{A}{k_d [K]}$$

As can be seen from Table 2, the rates of polymerization, R_p , were almost constant, except for nitro- and iodobenzene. As expected, nitrobenzene acted as an inhibitor for the polymerization of styrene. The

reason for the lack of polymerization observed in iodobenzene is discussed later.

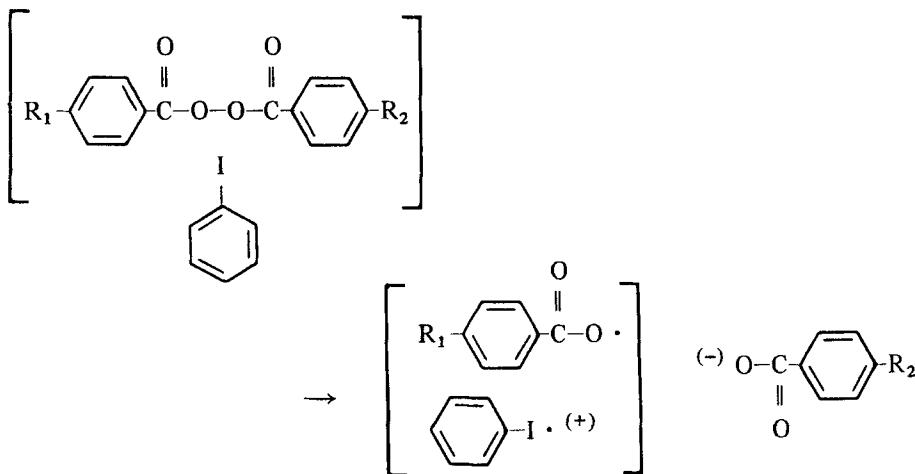
The unexpected constancy of R_p values, $2.11 \sim 2.45 \times 10^{-5}$ moles/liter sec, is attributed to a leveling effect of the initiation efficiency on the rate of polymerization. Even in cyanobenzene, in which the value of k_d is much larger than in other solvents, R_p reduced to a value similar to that of other solvents.

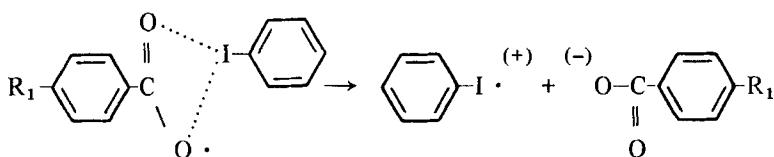
The degree of polymerization of polystyrene obtained by MN-BPO was generally smaller than that obtained by unsubstituted BPO. This may be explained by a chain transfer of the polystyryl radical to the p-nitrobenzoyl group of the initiator.

The Decomposition of MN-BPO with Iodobenzene

Since the value of f equals zero in iodobenzene, we are presented with an interesting problem. With regard to the decomposition reaction, the following considerations may be possible: (1) only an ionic decomposition proceeds with a very fast rate; (2) even if a radical decomposition occurs, the generated benzoyl radicals react with iodobenzene and few radicals escape from the solvent cage owing to a complex formation by the radical with iodobenzene.

Recently, Williams and co-workers [8] studied the decomposition of nonsubstituted BPO in a solution of benzene derivatives and proposed a σ -complex formation between the decomposed radical fraction and the solvent. According to them, the following mechanism might be considered in our case:





Thus, initiation of polymerization would not be expected. However, when an UV-spectroscopic measurement was carried out on the mixture of MN-BPO and iodobenzene, formation of a charge transfer complex could not be observed.

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